

THE USE OF COMPUTER SIMULATIONS TO INTERPRET AND UNDERSTAND ELECTRICAL MEASUREMENTS

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ABSTRACT

It is very rare to obtain complete 3-D information in the form of images of the microstructure of a material. Most often this information is incomplete because the resolution is inadequate, or is restricted to 2-D, via some kind of micrograph, or is not available at all. In the case of incomplete microstructural information, electrical measurements are then used to try to check a hypothesized microstructure, to see if it can account for the measured electrical response. But even when complete microstructural information is available, if the microstructure is random, then it is not possible to analytically calculate the electrical response of the microstructure. The use of computer simulations, both to generate material shape and topology and numerically solve the electrical equations, is then required. Computer simulations allow the use of more complex hypotheses for the microstructure of a material, as the electrical response can be accurately computed for a wide range of microstructural shapes and topologies.

INTRODUCTION

In materials science, there are really two uses for electrical measurements. The first is to see if a material has the proper electrical properties for a given application. The second use is the general one of trying to discover how the shape, topology, and electrical properties of material phases in a microstructure affect the overall electrical properties. This paper will focus on this second use of electrical measurements.

Sometimes a picture of the microstructure is available, but usually in 2-D and less often in 3-D, and sometimes not at all. When direct information about the microstructure is not available, usually a hypothesis is made about the microstructure, which can hopefully explain the overall electrical behavior seen. This depends on whether or not the electrical response of the hypothesized microstructure can be calculated. Agreement with the measured electrical properties lends support to the hypothesized microstructure. But even when direct images of the microstructure, in 3-D, are available, if randomness or complexity is present there is still a difficulty in knowing how to compute the electrical response. It is not an easy task to go from an image to the electrical response. The general task of going from a structure to an electrical response is especially difficult because the electrical response of a material depends not only on the shape and topology of the phases but also on the material properties of the individual phases.

The reason that this task requires computer simulations is that for many real shapes and topologies, especially in random materials, exact analytical equations cannot be developed. Complex hypotheses about microstructure, which are required for most real materials, are not useful when there is no way of exactly solving a complex hypothesized microstructure for its effective electrical properties. Simple hypotheses have been made that while often useful, cannot capture the full intricacies of a random microstructure. Computer simulations, as will be shown, can, within the limitations of

processing power and memory constraints, handle arbitrary shapes, topologies, and electrical properties. It is important to emphasize that the electrical response of a microstructure is indeed a mixture of shape, topology, and electrical properties. Two different topology microstructures can give a similar electrical response depending on the electrical properties of the different phases.

In this paper, "electrical properties" means DC conductivity, with the amplitudes of applied fields small enough so that the material response is always linear. The term "computer simulations" means direct construction of a microstructure in a computer, and then solution of the appropriate electrical equations on this microstructure under some set of boundary conditions. The main kind of simulation that will be discussed in this paper is typified by programs like *dc3df*, whose code and operating manual can be found at <http://ciks.cbt.nist.gov/garboczi/> [1]. This is a finite-difference program for DC linear 3-D steady-state conduction problems, where the microstructure is described by a digital image. This program is especially adapted for working on 3-D digital images. The problem being solved is given by the equation

$$\nabla \cdot (\sigma \vec{E}) = 0 \quad (1)$$

where the current flux density is given by

$$\vec{j} = \sigma \vec{E} \quad (2)$$

so that eq. (1) is the steady state charge conservation equation.

Besides studying random microstructures, one can also be concerned about particle shapes when a second phase is particulate. In the case of very small particles, it may be difficult to directly image them and so their shape must be inferred from property measurements. One can also be concerned about sample and electrode shape. Simple sample shapes are usually preferred, like cylinders, cubes, etc. because when the electrodes are applied uniformly across the ends, the applied field is uniform in the sample. However, it may be experimentally useful to have an "odd" sample and/or electrode shape. The electrical equations will usually not be analytically solvable for a general shape. In this case as well, computer simulations make it possible to understand the response of these kind of shapes. The remainder of this paper will show how computer simulations can be used at the individual particle level, the microstructural level, and the sample level, to compute the overall electrical signal.

INDIVIDUAL PARTICLE LEVEL

When a second phase is particulate, and is dilute, so that its volume concentration is small, say at most 5% or so, then much can be inferred about particle shape and electrical properties from the electrical signal. To be more specific, the case is that a second phase, of some conductivity σ_2 and volume fraction c_2 , embedded as isolated particles in a matrix of conductivity σ_1 and volume fraction c_1 . We wish to infer the shape and properties of the particles from the overall conductivity, where

σ_1 is known. In this case, much can be done analytically, for certain shapes.

The quantity to be discussed in this case is the *intrinsic conductivity*, $[\sigma]$, defined in the following way [2]:

$$[\sigma] \equiv \lim_{c_2 \rightarrow 0} \frac{(\sigma - \sigma_1)}{\sigma_1 c_2} \quad (3)$$

where σ is the measured conductivity. Equations (1) and (3) can be solved analytically for tri-axial ellipsoidal shapes (which includes spheres) for any value of σ_2 . In the limit of σ_2 being zero (insulating particle) or infinity (superconducting particle), other shapes can also be solved analytically [2]. Ref. [2] also shows how many different shapes can be solved numerically, via computer simulation, in the limits of an insulating or superconducting particle. A simple Padé approximant can then be used, along with the simulation or analytical results for the insulating and superconducting limits, to predict the intrinsic conductivity for any value of the relative conductivity σ_2 / σ_1 [3]. The intrinsic conductivity as a function of σ_2 / σ_1 can be also computed via simulation [3].

A simple shape whose intrinsic conductivity cannot be computed analytically is shown in Fig. 1a. This shape is formed from a unit cube but with an $m \times m$ ($m < 1$) square channel cut through the center of each face, leaving only a solid frame. Figure 1b shows a graph of the intrinsic conductivity of this object for $m = 0.941$, vs. its dimensionless conductivity, $x = \sigma_2 / \sigma_1$. In the insulating limit of x , the curve is fairly flat, going to a value of about -1.5. When x becomes very large, in the highly conducting particle limit, the value of the intrinsic conductivity also becomes quite large, around 50. In contrast, for a solid cube or sphere, this limit is only about 3 [2]. Figure 1c shows a linear-log graph of the intrinsic conductivity of the particle, in the superconducting limit, denoted $[\sigma]_\infty$, as a function of the empty air portion of the unit cube from which the particle is made. The air volume fraction of the particle is simply given in terms of m by

$$\text{Air volume fraction} = m^2 (3 - 2m) \quad (4)$$

The intrinsic conductivity goes up rapidly with the empty air portion of the particle, becoming very large as the value of m approaches one and the particle shape approaches a wire frame, since the volume fraction of the object, c_2 , becomes very small while the particle still has an appreciable effect on the overall conductivity, so that eq. (3) become large.

If one has no idea what the shape of a second phase particle might be, then it is difficult to use the simulation and analytical results, as there are many combinations of shape and σ_2 / σ_1 that can agree with the measured results. However, if one has a hypothesis about the particle shape and electrical properties, then these kind of results can be used as a quantitative test of the hypothesized shape and electrical properties of the second phase. There are many other references in Refs. [2] and [3] that

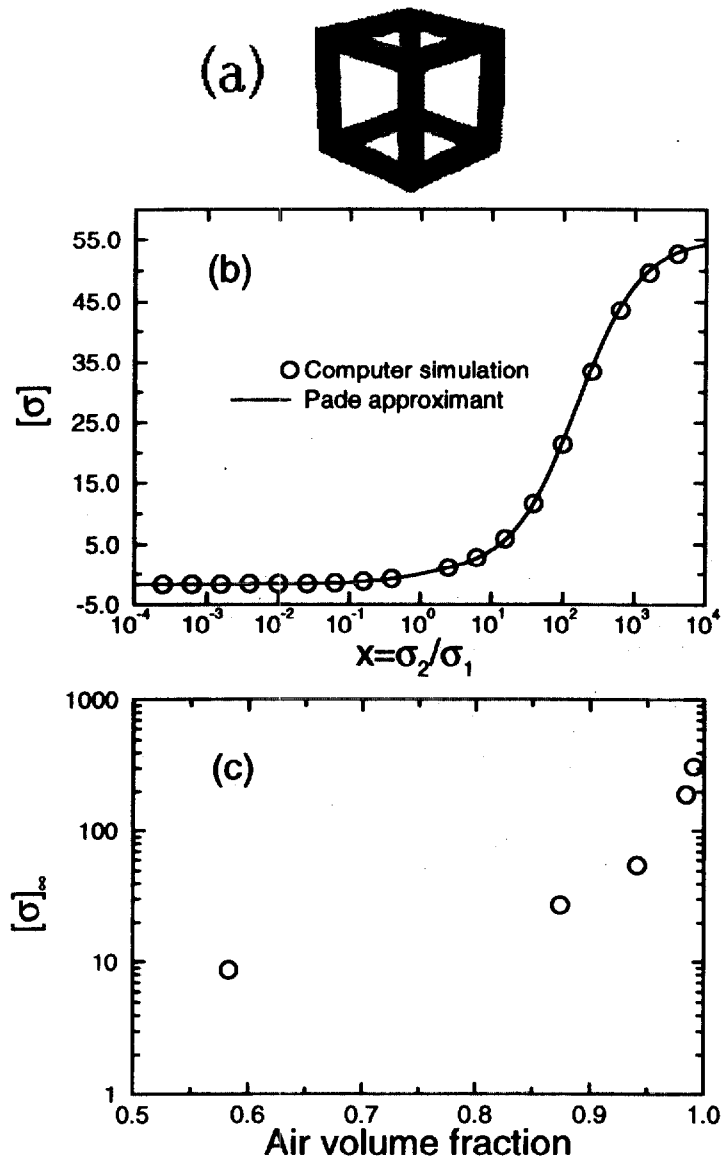


Figure 1: (a) particle shape, (b) intrinsic conductivity of object with $m=0.941$ vs. ratio of object conductivity to matrix conductivity, and (c) intrinsic conductivity of object in the highly conducting limit, vs. the air content of the object.

detail uses of these results in materials science, and particularly polymer science, where this method of inferring particle properties is commonly employed. One should note that if x is close to 1, then the intrinsic conductivity is rigorously known to be insensitive to particle shape [3]. Also, when $x \ll 1$, the intrinsic conductivity is also not very sensitive to particle shape [3], so in these two regimes, determining particle shape from the electrical response would be an even more difficult task.

MICROSTRUCTURAL LEVEL

At the microstructural level, we wish to see if a hypothesized microstructure can produce the measured electrical response. For non-dilute volume fractions or for topological connection of a phase throughout the material (percolation), exact analytical formulas, except in very special cases, are impossible to produce. These special cases include the case when the phases in a microstructure are exactly aligned in series or parallel behavior, or when they follow one of the "ideal" microstructures represented by the Hashin bounds [4]. For random materials, this almost never happens, so that simple hypothesized microstructures, whose electrical responses can be calculated analytically, are not very useful. However, if one produces a complex hypothesized or model microstructure via computer simulation, and then uses computer simulation again to compute the electrical response, progress can be made in understanding the material.

An example of this approach is from cement paste, which is a combination of portland cement and water, that changes from a viscous suspension to a rigid solid via hydration reactions between the solid phase and the water. The solid particles are on the scale of 10-20 μm , and so the pore space, the water-filled space between the particles called the capillary pore space, is also at this scale. The solid phase grows, because the reaction products are less dense than the cement, so that water is consumed as the initial pore space is filled up, resulting in a porosity that decreases with time. The electrical properties come from the fact that the water contains dissolved ions from the cement, making the pore space a conductor. The main reaction product, called CSH, is also porous on the nanometer scale, so that even as it fills up the capillary pore space, it creates a nano-porous network which is also filled with aqueous electrolyte.

Models have been made of this material in 3-D that closely mimic the evolving microstructure. By computing the electrical properties of this model [5-7] one can compare model predictions to experiment and extract information about the microstructure. Figure 2 shows a slice from such a 3-D model, where (a) shows a slice from the simulated microstructure, and (b) shows the electrically conductive phases colored white and gray, and all the insulating phases colored black. There are two conducting phases, the capillary pore space, with a given conductivity (white), and the nano-porous CSH, which is treated as a uniform conductor at the micrometer scale.

At room temperature, the conductivity of the capillary pore space dominates the overall conductivity. It is possible to measure the conductivity of the pure capillary pore space by squeezing out the pore water and measuring its conductivity separately [5]. However, it is not possible to prepare CSH by itself that is equivalent to its form inside the cement paste. There is also no way, in this random material, to analytically extract the two separate conductivities from the overall conductivity.

By using the above model, which gives an accurate description of the microstructure, and comparing

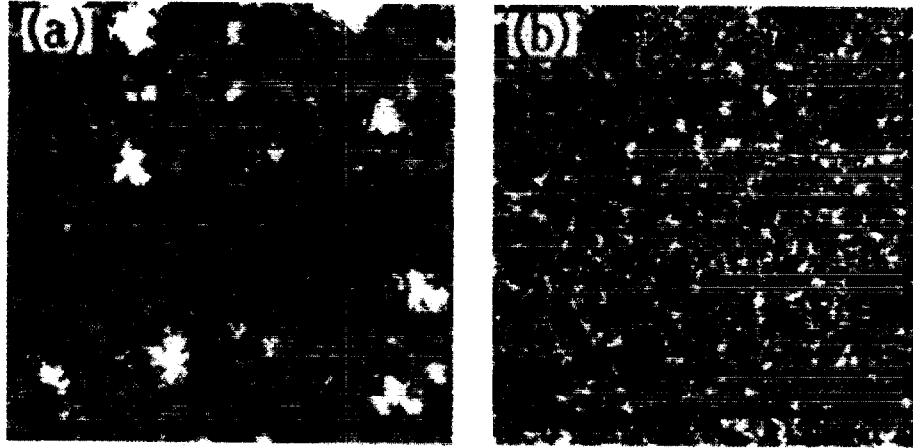


Figure 2: (a) model cement paste microstructure (black = capillary pores, white = unreacted cement, dark gray = CSH, light gray = other insulating reaction product), and (b) map of electrical conductivity (white = capillary pores, gray = CSH, black = insulating phases).

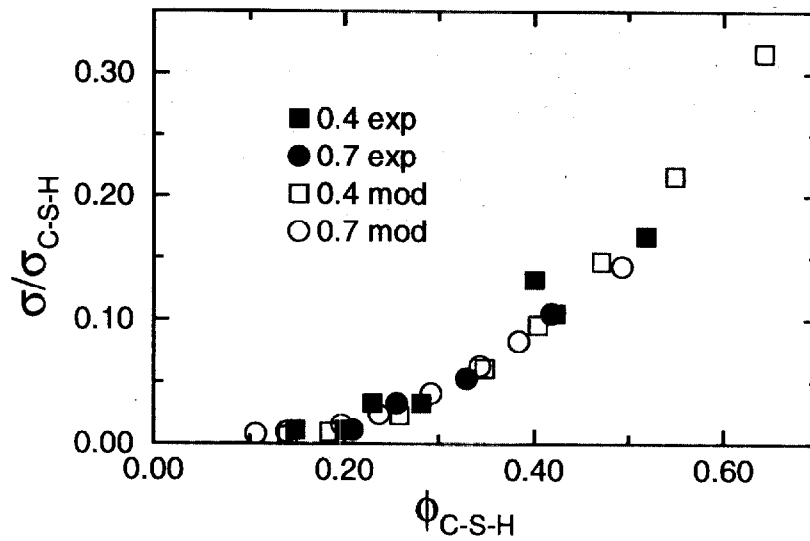


Figure 3: Conductivity at -40°C normalized by the conductivity of the pure CSH phase, for two different cement pastes, mixed with different amounts of cement and water.

to experiment, a fairly accurate value of the conductivity of the CSH phase relative to that of the capillary pore space was obtained [5-7]. In the model, the capillary pore space is given a conductivity of unity, so that the computed conductivity will be relative to the capillary pore space value. Experimentally, the capillary pore space conductivity is measured, as described above, and the overall conductivity normalized by this value. The model is then used to compute the overall conductivity for a range of chosen CSH conductivity values. By matching to experiment, the value of the CSH conductivity at room temperature was found to be about 0.0025-0.01 relative to the capillary pore space [5-7].

When the temperature is lowered below the freezing point of water this situation reverses [8]. By lowering the temperature to -40°C , the water in the larger micrometer scale pores is frozen, while the water in the nanometer scale CSH pores is still mobile. This switches the conductivities of the two phases, even though both are lower than at room temperature, so that now the CSH phase has about 100 times the conductivity of the capillary pore space and has become the dominant conducting phase. However, like at room temperature, the absolute value of the conductivity of the pure CSH is not separately measurable. Using the cement paste model, simulations were run of the frozen cement paste conductivity, normalized by the (unknown) CSH conductivity. This was done by assigning a conductivity of unity to the CSH, and 0.01 to the capillary pore space, and then running the model. These were run for two different combinations of water and cement (ratio of the water mass to the cement mass of 0.4 and 0.7). These results were then compared to experimental data. It was found that by choosing a certain value for the frozen conductivity of the CSH phase, and normalizing the experimental data by this value, the simulation and experimental results agreed very closely. These results are shown in Figure 3. The model also predicted a percolation threshold of about 15% volume fraction for the CSH phase, which is confirmed by Fig. 3. At this temperature, the CSH phase is by far the main conducting phase, so that the conductivity goes approximately to zero at the CSH percolation threshold, which in this case is the signature of the percolation threshold.

This kind of comparison between experiment and model results was also done for electrical measurements at frequencies up to about 10^7 Hz, with some degree of success [9]. See Ref. [9] for details of this work, and Ref. [1] for the details of the computer programs, equivalent to *dc3df*, that can be used at finite frequencies.

SAMPLE STRUCTURE LEVEL

In a simple experimental set-up, a cylindrical sample with electrodes covering both ends fully, one can assume that the applied field is uniform over the sample, and it is then easy to convert measured resistances into resistivities or conductivities. Often, however, in electrical experiments, the geometry of the sample or of the applied electrodes is an experimental variable. In this case one cannot simply assume that the applied field is uniform. In these cases, if the material property is known, the effect of the sample and electrode geometry can be predicted via computer simulation, to see quantitatively what effect this geometry has on the results. This use of computer simulation has been carried out recently in a case involving variable electrode geometry.

This case occurred in a study of the effect of electrode geometry on three-point measurements [10,11]. In this kind of measurement, the *working* and *counter* electrodes are used to apply an

electrical signal, and the complex voltage is sensed at the *reference* electrode for the purpose of looking at the material-electrode response. The geometry of the working and counter electrodes, and the geometry and position of the reference electrode, was varied across typical experimental geometries to see what effect this might have on properly measuring material-electrode impedances. The samples were cylindrical with a circular cross-section, with the electrodes applied across the ends of the sample. Figure 4 shows two electrode configurations that were investigated numerically, out of the many that were investigated experimentally [10,11]. The electrical field was applied across the CE and WE, and the impedance was measured at the RE. Using a 3-D digital image, the sample and electrode geometry were duplicated, and the impedance response at a number of frequencies was simulated using a finite difference technique applied to the digital image [1,9]. In the computer simulations, a known material-electrode response was used, so that artifacts from the electrode arrangements could be readily seen.

Clear differences were seen experimentally between different electrode arrangements. These artifacts, due to electrode geometry, were confirmed by the computer simulation results. The true material-electrode response, for some arrangements of the electrodes, was not seen because of these distortions. The electrode arrangements, although simple, were such that analytical solutions of eq. (1) were not possible, so that computer simulation played a vital role here in correctly interpreting experimental results. Simple guesses of how a certain electrode configuration would respond turned out to be very misleading. Only computer simulation could be used to sort out the experimental artifacts from the true response.

In some situations, it would be experimentally convenient to have a non-uniform arrangement of electrodes and/or sample shape. This is usually not done because the applied field would not then be uniform. The availability of these computer simulation techniques alleviates this difficulty and makes it possible to be more flexible with electrode and sample shapes.

DISCUSSION

One point that needs further discussion is the electrical signature of a percolation threshold in a material. The connectivity of a phase is important information, and the electrical response is often looked to for obtaining this information. Even after restricting the discussion to two phases, there is still an interplay between two factors: (1) the actual geometrical percolation of either phase, and (2) the electrical conductivity contrast between the two phases, $x = \sigma_2 / \sigma_1$.

Suppose that it is geometrically possible that both phases can become percolated. This will be the case in a material like cement paste, as described above, or in a two-phase polymer blend, or in a random interpenetrating phase ceramic composite [12]. Consider the case when phase 2 is not percolated, but is becoming percolated through some sort of chemical or physical process. Will the percolation of phase 2 be seen in the electrical conductivity of the material? That depends on the value of x . If x is on the order of 100 or more, there will be a sharp upturn in the overall conductivity when phase 2 percolates, thus giving the signature of the percolation threshold (volume fraction of phase 2 at percolation). If x is between 1 and 10, a sharp upturn will not be seen, but only a fairly gradual increase, which will not pick out a percolation threshold. For values between 10 and 100, there may or may not be a sharp increase, depending on the microstructure. For values of x less than

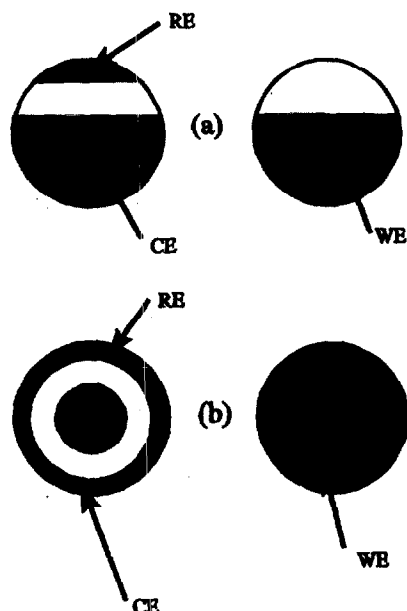


Figure 4: Showing two different experimental electrode arrangements that were investigated via computer simulation [(a) and (b)]. Electrodes are applied to ends of samples, gray = metallic electrode, WE = working electrode, CE = counter electrode, and RE = reference electrode.

one, even for $x = 0$, nothing will be seen as in 3-D the percolation of one phase does not require the disconnection of another phase. The percolation of phase 2, which is insulating in the case of $x = 0$, will only decrease the overall conductivity and will not give a sharp downturn. So unless x is large, the geometrical percolation of phase 2 will not have a signature in the conductivity.

This fact is an important point to remember. Suppose one has a material with a second phase in it that one thinks may be becoming percolated. If a percolation threshold is not seen in the electrical conductivity, as denoted by a sharp upturn in the conductivity, phase 2 may be percolated and yet have a low value of x , or it may not be percolated and have a fairly high value of x . Or, if the conductivity is decreasing as the volume fraction of phase 2 increases, it certainly means that x is less than unity, but it does not say anything about the percolation aspects of phase 2.

Another point that should be mentioned concerns the use of approximate analytical expressions like effective medium theories. These theories are typically some sort of formula that is exact in the dilute limit, with statistical ideas used to approximately extend this exact result to general volume fractions. These equations can often work quite well in describing the overall electrical conductivity. This success should not be pushed too hard, however. Remember that the electrical response of a phase is some combination of its shape and topology *and* its individual electrical properties. For example, the above discussion of percolation shows that unpercolated and percolated phases can give the same electrical response, depending on their individual electrical properties relative to the rest of the material in which they are contained. An approximate equation mixes together the geometrical and electrical properties of the phase in some algebraic way that may be much different from reality. If one tries to "deconvolute" an approximate equation to extract the value of volume fraction or electrical property or shape for a given phase, especially a minor phase, the answer one gets can be seriously in error. An example of this kind of error is given in Appendix A of Ref. [13].

CONCLUSION

A calculation must be made of the electrical response of either an hypothesized model for the microstructure, or of an actual 3-D image obtained experimentally. This calculation involves the shape, topology, and electrical properties of each material phase. Unless the phases are arranged in a simple arrangement, which is not usually the case for real (random) materials, this calculation cannot be made exactly by analytical methods. Computer simulation is useful in this case for computing the electrical response. Computer simulation is also useful for considering individual particles whose shape precludes exact analytical methods, and for handling sample and electrode shapes and arrangements where analytical methods also fail.

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